Supporting Information for

Fluorous-Phase Ion-Selective pH Electrodes: Electrode Body and Ionophore Optimization for Measurements in the Physiological pH Range

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1. Characterization of the Fluorophilic Ionophore N[CH₂CH₂CH₂CH₂R$_{f8}$]₃ (2)
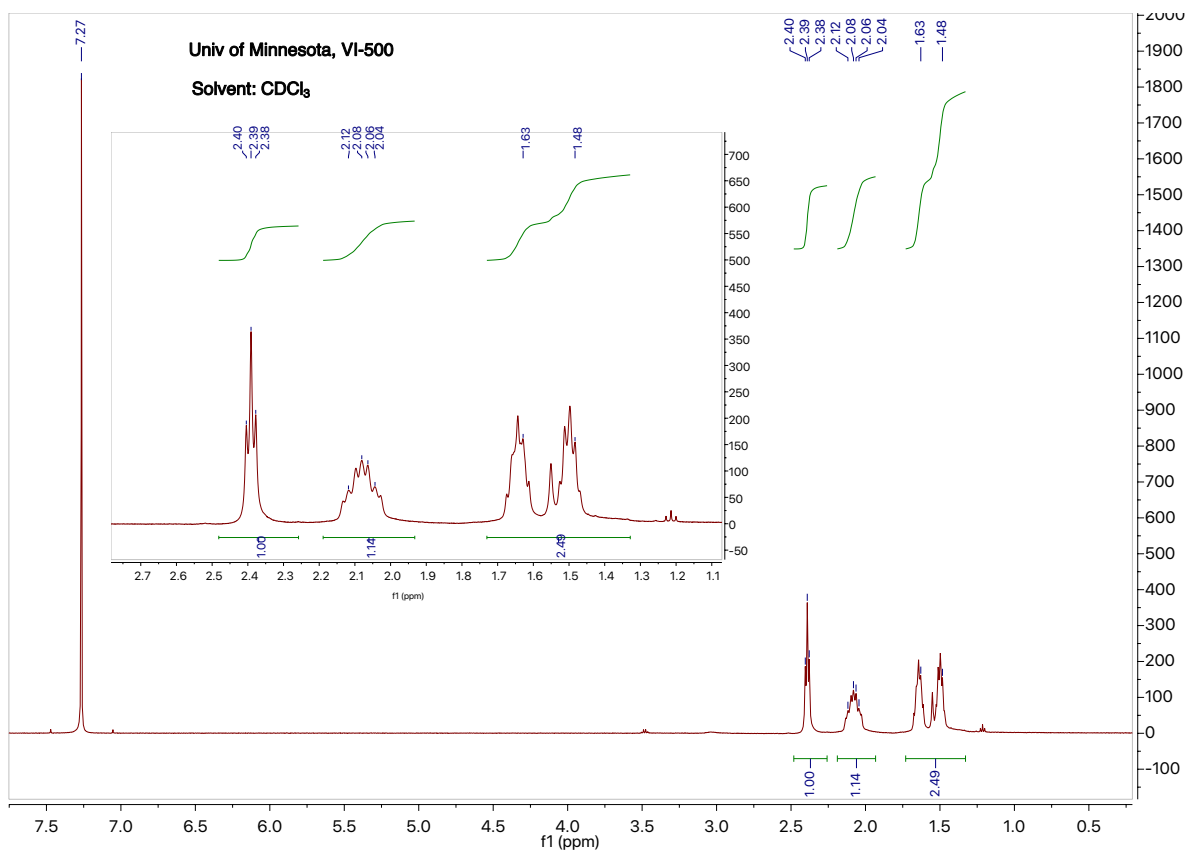
Figure S1. ^{1}H NMR spectrum of the fluorophilic ionophore N[CH₂CH₂CH₂CH₂R$_{f8}$]₃ (**2**).

Intens.

1440.1

+MS
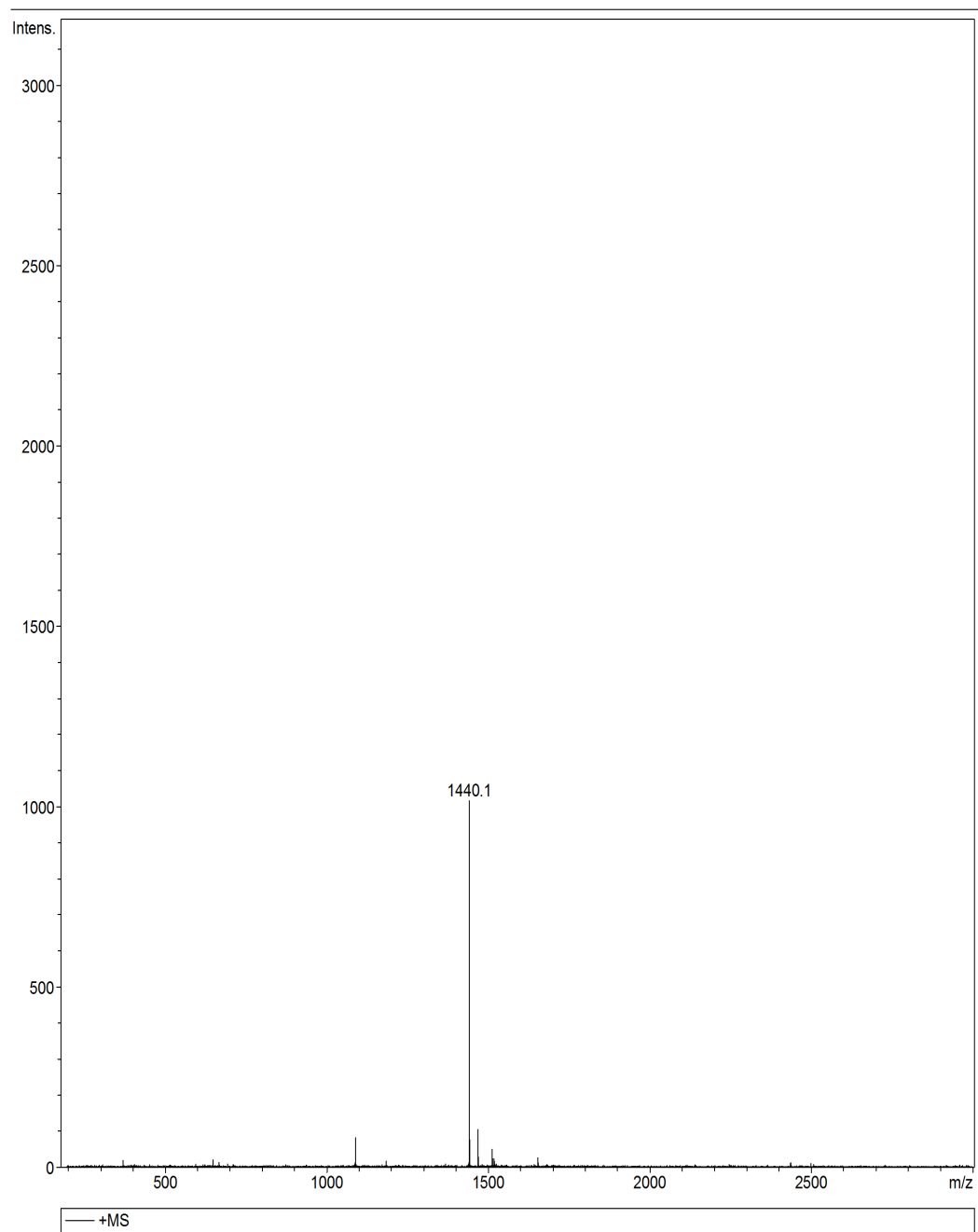
Bruker Daltonics DataAnalysis 3.4

Electrospary - TOF

Figure S2. Electrospray mass spectrum of the fluorophilic ionophore $N[CH_2CH_2CH_2CH_2R_{f8}]_3$ (**2**).
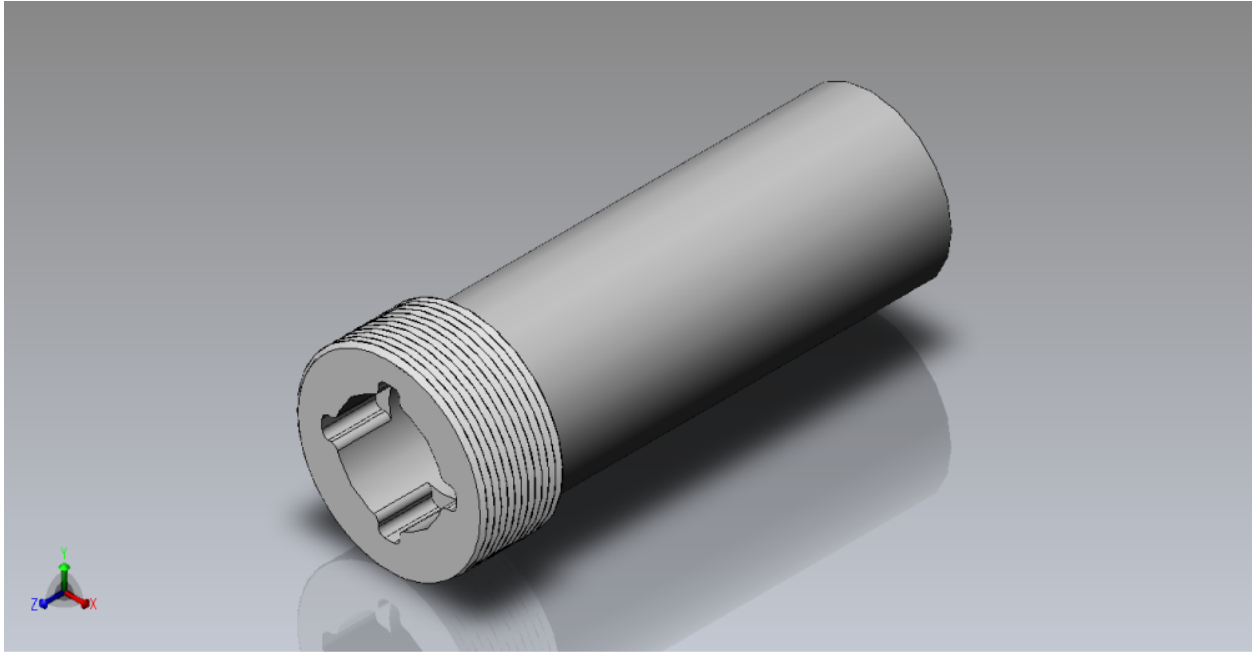
2. Design of the Electrode Body

Figure S3. 3D view of outer electrode body piece (upper end shown in front). Four locking slots (at 90º to each other) securely hold the lugs of the inner electrode body piece (see Figs. S4 and S5), preventing the inner body piece from rotating within the outer electrode body piece when the screw cap is mounted.
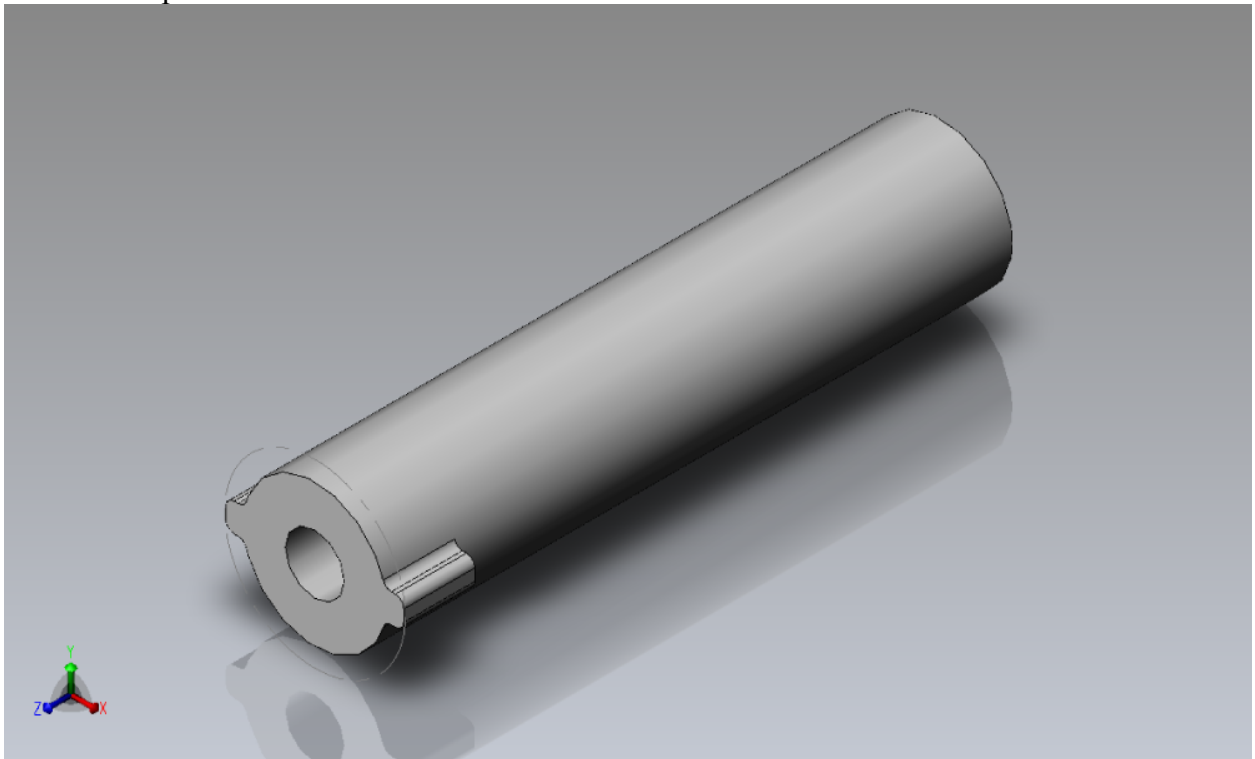

Figure S4. 3D view of inner electrode body piece (upper end in front). Two lugs (at 180º to each other) securely fit into locking slots of the inner electrode body piece (see Figs. S3 and S5).
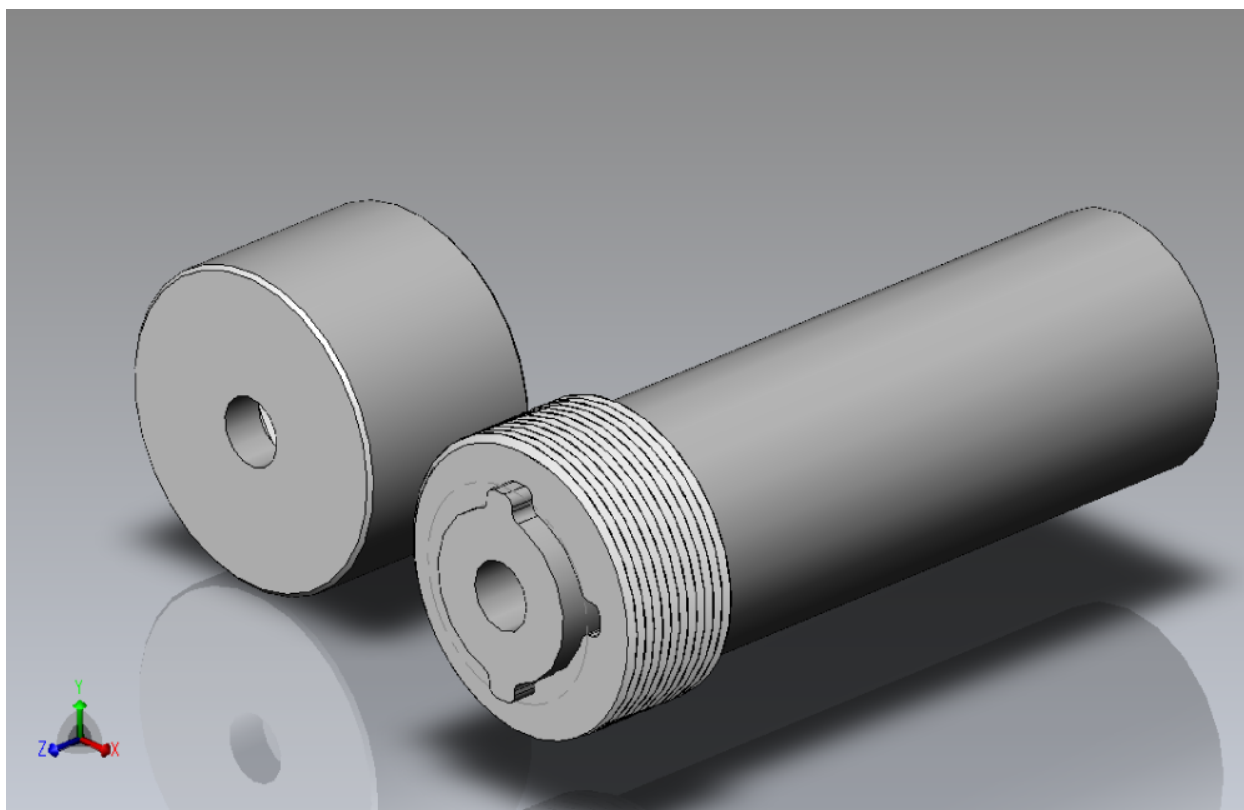
Figure S5. 3D view of screw cap (left) and the inner electrode body piece mounted inside the outer electrode body piece (right). The two lugs of the inner electrode body piece fit into the locking slots of the outer body piece. When the cap is screwed onto the outer body piece, it exerts pressure onto the inner body piece, pushing it onto the sensing membrane (located between the inner and outer body pieces) without causing any rotating motion of the membrane. This ensures a tight and smooth mechanical seal of the membrane.
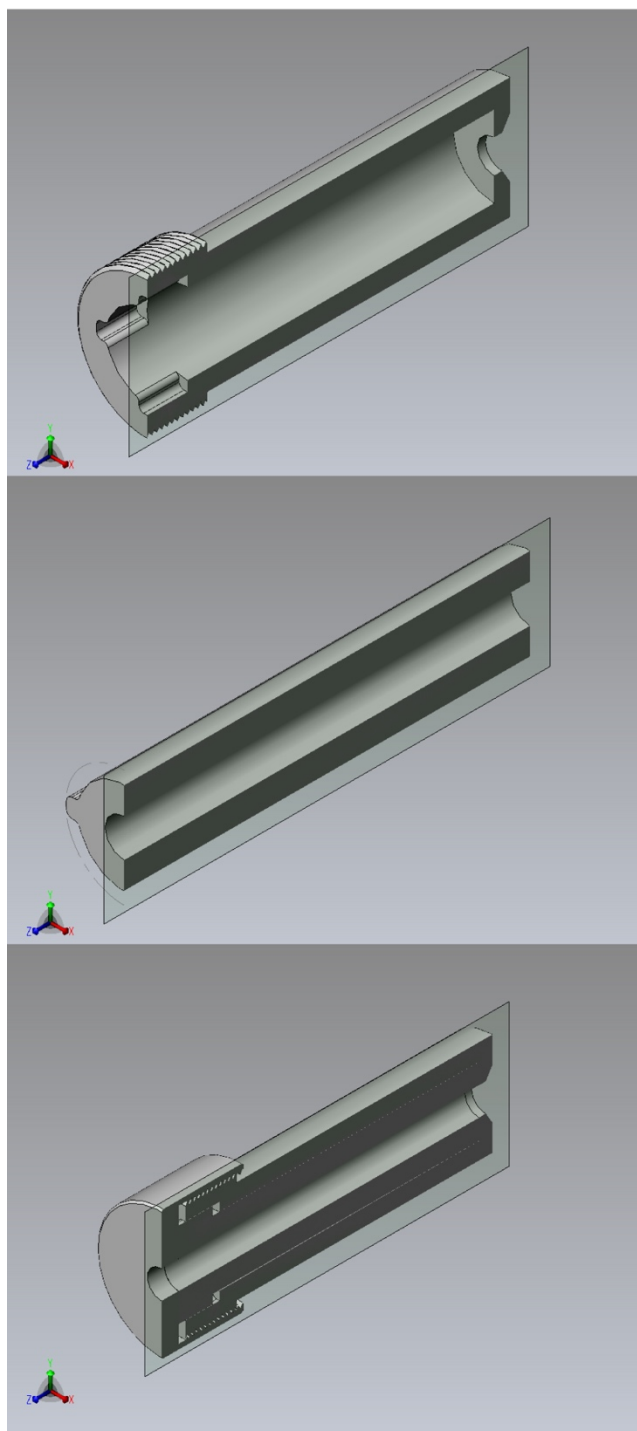
Figure S6. 3D views of cross-sections of the outer electrode body piece (top), inner electrode body piece (middle), and the whole assembly with the screw cap (bottom).
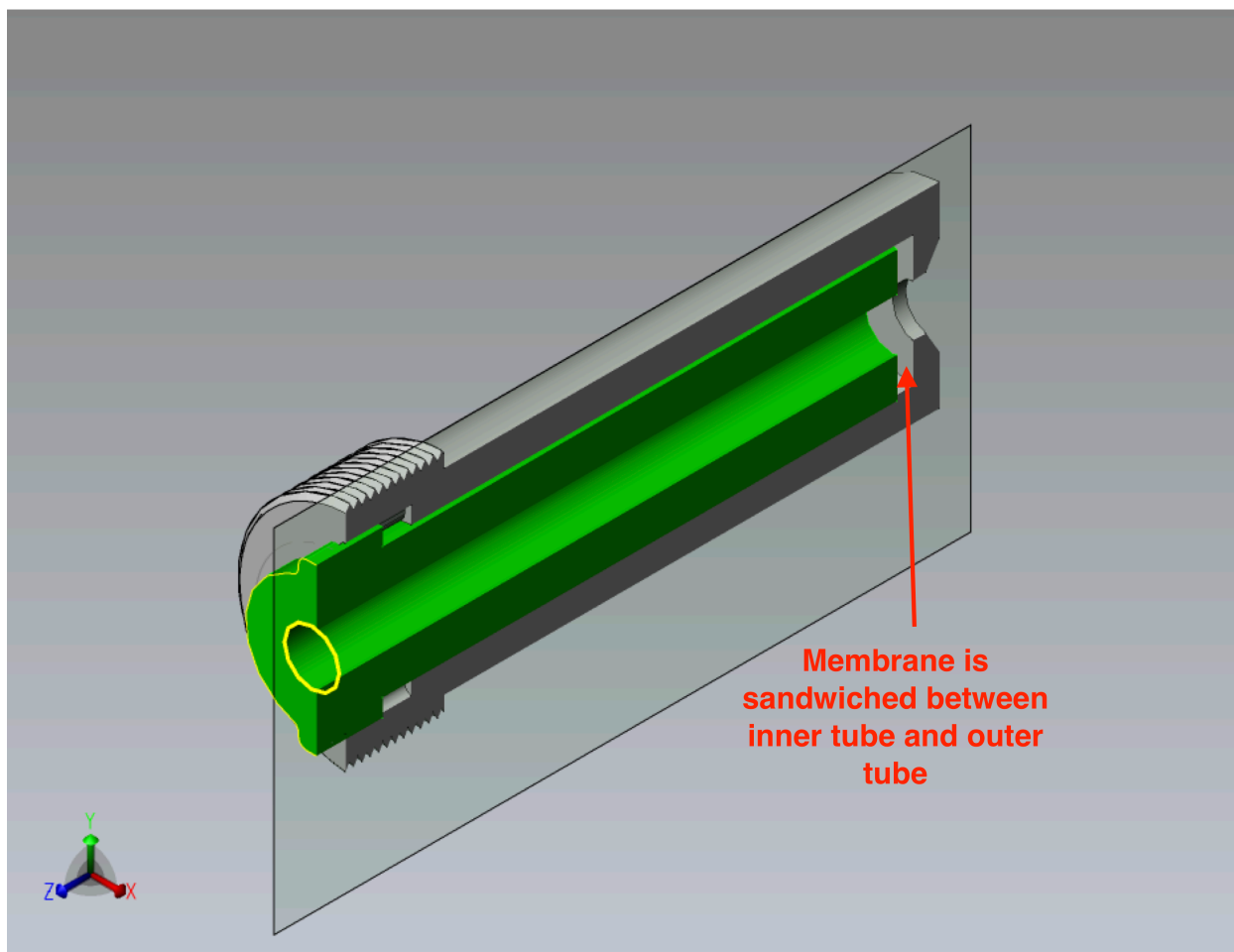
Figure S7. 3D view of a cross-section of the inner and outer electrode body pieces, illustrating where the membrane is located.
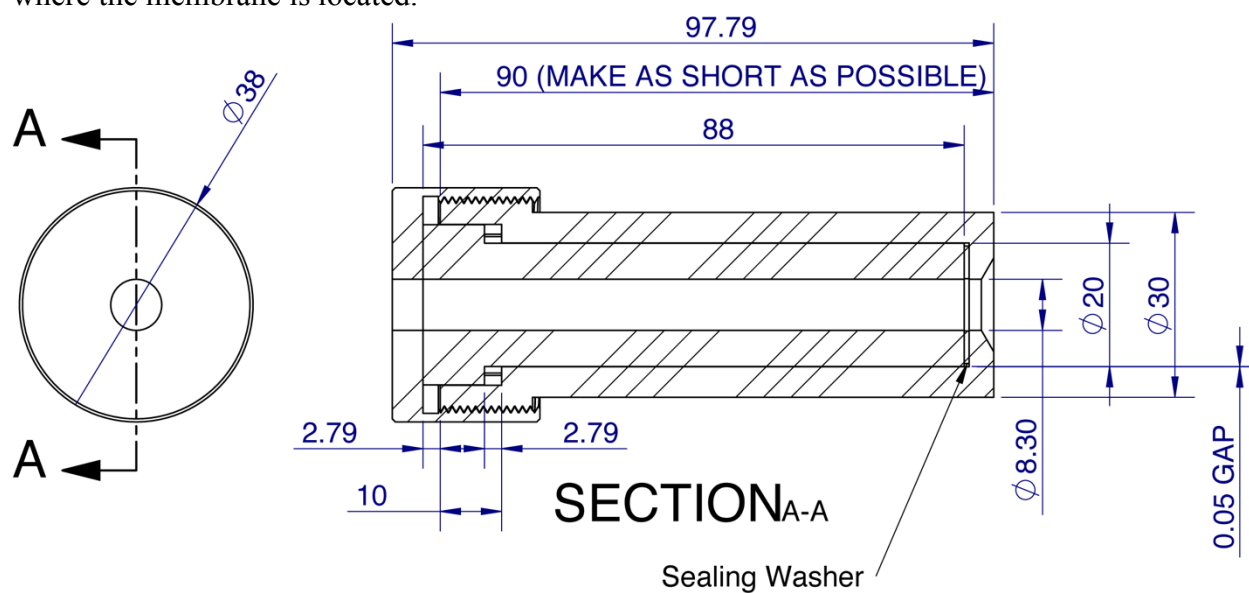

Figure S8. Detailed dimensions of the electrode body (unit: mm).

3. Selectivity Measurements

The non-coordinating reference ion considered initially for the determination of the pK_a of

$N[CH_2CH_2CH_2CH_2R_{f8}]_3$ in the fluorous phase was the tetraphenylphosphonium ion (PPh_4^+).

However, direct measurements of selectivities for PPh_4^+ with respect to H^+ failed because in such

experiments PPh_4^+ and H^+ did not give the required Nernstian responses. Therefore, it was also

attempted to determine this selectivity coefficient using a "selectivity ladder", i.e., by measuring

the SSM selectivities for NPr_4^+ and NBu_4^+, which exhibit selectivities intermediate between H^+

and PPh_4^+. Then, the selectivity for PPh_4^+ with respect to H^+ was computed with eq S1:

$$\log K_{H,PPh_4}^{pot} = \log K_{H,NPr_4}^{pot} + \log K_{NPr_4,NBu_4}^{pot} + \log K_{NBu_4,PPh_4}^{pot} \qquad (S1)$$

The pK_a value determined for ionophore **2** on the basis of $\log K_{H,PPh_4}^{pot}$ and eqs 2 and 3 was 15.8 ±

1.2, which is higher than the value previously reported for ionophore **3** with $-(CH_2)_5-$ spacers

(15.4). This is likely due to errors associated with the indirect measurement of multiple

selectivity coefficients using the selectivity ladder approach. In the measurement of each of these

selectivity coefficients, intercepts of calibration curves are used to calculate selectivity

coefficients. Therefore, errors may come from Nernstian slopes ranging between 56 and 63

mV/decade, which affect intercepts and propagates errors into $\log K_{H,PPh_4}^{pot}$.